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Biogeosciences Discussions, 2, 1381–1422, 2005
www.biogeosciences.net/bgd/2/1381/
SRef-ID: 1810-6285/bgd/2005-2-1381
European Geosciences Union

Biogeosciences Discussions is the access reviewed discussion forum of *Biogeosciences*

Nitrogen oxides emission from two beech forests subjected to different nitrogen loads

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Received: 1 July 2005 – Accepted: 13 July 2005 – Published: 9 September 2005

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Abstract

We analysed nitrogen oxides (N_2O, NO and NO_2) and carbon dioxide (CO_2) emissions from two beech forest soils close to Vienna, Austria, which were exposed to different nitrogen input from the atmosphere. The site Schottenwald (SW) received 22.6 kg N y^{-1} and Klausenleopoldsdorf (KL) 13.5 kg N y^{-1} through wet and dry deposition. Nitrogen oxide emissions from soil were measured hourly with an automatic dynamic chamber system. Daily N_2O measurements were carried out by an automatic gas sampling system. Measurements of nitrous oxide (N_2O) and CO_2 emissions were conducted over larger areas on a biweekly (SW) or monthly (KL) basis by manually operated chambers. We used an autoregression procedure (time-series analysis) for establishing time-lagged relationships between N-oxide emissions and different climate, soil chemistry and N-deposition data. It was found that changes in soil moisture and soil temperature significantly effected CO_2 and N-oxide emissions with a time lag of up to two weeks and could explain up to 95% of the temporal variations of gas emissions. Event emissions after rain or during freezing and thawing cycles contributed significantly (for NO 50%) to overall N-oxides emissions. In the two-year period of analysis the annual gaseous N_2O losses at SW ranged from 0.65 to 0.77 kg N ha^{-1} y^{-1} and NO losses were 0.18 to 0.67 kg N ha^{-1} per vegetation period. In KL significantly lower annual N_2O emissions (0.52 kg N_2O-N kg ha^{-1} y^{-1}) as well as considerably lower NO-losses were observed. During a three-month measurement campaign NO losses at KL were 0.02 kg, whereas in the same time period significantly more NO was emitted in SW (0.32 kg NO-N ha^{-1}). Higher N-oxide emissions, especially NO emissions from the high N-input site (SW) indicate that atmospheric deposition had a strong impact on losses of gaseous N from our forest soils. At KL there was a strong correlation between N-deposition and N-emission over time, which shows that low N-input sites are especially responsive to increasing N-inputs.

1. Introduction

Nitrogen emissions are driven by soil substrate, tree species, climate, short term fluctuations of water availability as high rain, freeze thaw cycles and atmospheric inputs (e.g. Dahlgren and Singer, 1994; Fitzhugh et al., 2001; Lovett et al., 2002; MacDonald et al., 2002). The effect of N-deposition on N-emissions has become a major issue due to the observation of a significant worldwide increase in N-deposition rates; a further increase is predicted as a result of an increased use in fertilizers and increased energy consumption (Galloway et al., 1995; Hall and Matson, 1999). In forest ecosystems increased N supply results in N saturation which is indicated by increased N-leaching from soils, soil acidification, forest decline, nutrient imbalances and losses, and soil emissions of N oxide gases (Gundersen et al., 1998; van Breemen et al., 1988; Aber et al., 1998; Skiba et al., 1999). Where N constitutes a limiting factor, competition between roots and microbes is high and nitrate (NO_3^-) is taken up. This is contrary to a high N supply which leaves ammonium (NH_4^+) and NO_3^- accessible for nitrifying and denitrifying bacteria. Chemodenitrification, nitrification and denitrification are the main sources of N-oxides emissions (Davidson, 1993; Venterea et al., 2003). Forest ecosystems with N-inputs exceeding critical loads have been found to accumulate N in soil (Beier et al., 2001). However, studies in N-saturated forests in Central (Zechmeister-Boltenstern et al., 2002; Butterbach-Bahl et al., 1997; Brumme and Beese, 1992) and Northern Europe (Pilegaard et al., 1999) have shown that N-saturated forests release significantly higher N_2O and, especially NO emissions, than N-limited temperate forests (Davidson and Kingerlee, 1997).

In the vicinity of cities or intensively managed agricultural lands, N-input can amount up to 50 kg N ha^{-1} y^{-1} (NADP, 2002; Tietema, 1993). Since there are only a few studies that investigated the effect of different N-deposition on forest ecosystems under similar climatic conditions (Hahn et al., 2000; Rennenberg et al., 1998; Skiba et al., 1998; Butterbach-Bahl et al., 2002a) our aim was to assess the influence of N-deposition on N_2O and NO_x emissions at two similar forest sites. Our approach included: (1) Field

measurements of CO_2, N_2O and NO_x emissions from soils of two beech forests with different N-deposition loads. Additionally, measurements were made in high temporal and spatial resolution (2) to get better estimates of annual emission (3) to study the effects of climatic factors and soil parameters on gaseous soil emissions and (4) to find an appropriate statistical procedure to describe the relationships between N-emissions and their ecological drivers.

2. Material and methods

2.1. Investigation sites and soils

The experimental site Schottenwald (SW) is situated in direct vicinity of Vienna on a SE-exposed upper slope in a 142 year old beech stand. The soil is a moderately well drained dystric cambisol over sandstone. In spring the undergrowth is dominated by a dense cover of the geophyte *Allium ursinum* L. changing to bare soil in summer and autumn. The second sampling site, Klausenleopoldsdorf (KL), is located about 40 km south-west of Vienna on a NNE-facing slope. On site there is a 62 year old beech forest growing on a dystric cambisol displaying no significant changes in ground vegetation throughout the year. For site description see Table 1.

2.2. N_2O and CO_2 flux measurements

We used the closed chamber technique in order to cover the spatial variability of N_2O and CO_2 soil emissions. Gas emissions were measured by manual (4/site) and automatic chambers (1/site). A manual chamber consists of an aluminium frame ($1 \times 1 \times 0.05$ m), which we inserted into the soil to a depth of 3 cm. A single-wall rigid polyethylene light-dome (Volume: 80 l) with a compressible PTFE seal at the bottom was fixed onto the aluminium frame by means of 4 screws. Duplicate air samples were taken from the chambers with 60 ml polypropylene gas-tight syringes at an interval of

0, 1 and 2 h. This procedure has been shown to allow realistic N_2O emission estimates for forest soils (Zechmeister-Boltenstern et al., 2002). 30 ml of the gas-probe were injected into evacuated and gas tight headspace vials (20 ml), fitted with a silicon sealed rubber stopper and an aluminium cap. Samples were taken on a biweekly (SW) or monthly (KL) basis from April 2002 until May 2004.

For the measurement of short-time temporal variations (1/day) of N_2O emissions an automatic gas sampling system (AGPS-patent DE 198 52 859) was used (UIT GmbH, Dresden). It consists of the following main components (Fig. 1): A covering case (1×1 m) with a rubber gasket, a slipping clutch for automatically closing and opening of the chamber and a thermostat. Within the protection case a fraction collector with 40 headspace vials (20 ml), a control system; a vacuum pump and a memory programmable control unit with the possibility of the free determination of the sampling times; an automatic needle plug-in with a double needle; the power supply that is provided either by batteries (2×12 V/DC) (at KL) or by existing power supply lines (at SW) where a mains adapter EP-925 (230 V to 24 V/DC) was interposed.

During sampling procedure the covering case glided across to the side of the sealing plate, thus, case-tightening the chamber for 70 min. During closure time air samples were extracted (flow rate ca. 100 ml min^{-1}) from the chamber by a membrane pump and transported through 10 m Teflon tubes to the vials. Sample lines and vials were flushed for 10 min before samples were taken from the headspace air of the chamber. Within these 70 min two gas samples were taken: The first one after 10 min, the second one after 70 min closure time. Automatic sampling was scheduled for 6 a.m. as in a previous experiment highest emission was measured at morning dew. During winter time measurements took place at 1 p.m., thus, avoiding night/morning frost. In order to prevent the covering case from freezing on the sealing plate the thermostat was set at 1°C and no measurements were conducted below this temperature.

The vials with the gas samples were stored at 4°C under water for 14 days maximum. In the laboratory gas samples were analysed for N_2O by gas chromatography (HP 5890 Series II) with a ^{63}Ni-electron-capture detector (ECD) connected to an au-

tomatic sample-injection system (DANI HSS 86.50, HEADSPACE-SAMPLER). Oven, injector and detector temperatures were set at 120°C, 120°C and 330°C, respectively. N_2 in ECD-quality served as carrier-gas with a flow rate of 30 ml min^{-1}. The gas-chromatograph was routinely cross-calibrated with a calibration gas of 5 μl l^{-1} N_2O (Linde Gas). CO_2 was analysed through a gas chromatograph (Hewlett-Packard 5890 II series) equipped with a thermal conductivity detector (TCD). Helium was used as carrier-gas (flow rate 10 ml min^{-1}); the CO_2 calibration gas contained 10 ml l^{-1} CO_2 (Linde Gas).

Emissions of N_2O (μg N m^{-2} h^{-1}) and CO_2 (mg C m^{-2} h^{-1}) were determined by the linear increase of the mixing ratio within the headspace of the closed chamber. The calculation of N_2O and CO_2 fluxes is described in the manual on measurement of CH_4 and N_2O emissions from agriculture (IAEA, 1992).

2.3. NO flux measurements

NO and NO_x exchange was directly measured on site using a chemoluminiscence detector (Holtermann, 1996). The detection limit of the NO_x-analyzer (HORIBA APNA-360) was 1 ppbv NO. Air samples were taken from six chambers connected to the NO_x-analyzer via PTFE tubing (inner diameter: 4 mm; length: 10 m). One of the six measuring chambers was used as a reference chamber by sealing the opening to the soil through a Plexiglas pane. The chambers were closed for 5 min when steady state was reached. Since there was no ozone analyzer available in 2002, the chamber inlets were supplied with clean air. For this ambient air was passed through a filter cylinder filled with Purafil and activated charcoal (length: 465 mm; diameter: 85 mm). Calibration was carried out through span gas (UBA certified) of a NO concentration of 153±2% ppb. Zero air preparation consisted of a bottle of compressed synthetic air (Cn Hm<0,1 vpm and NO_x<0,1 vpm). In 2002, the flux rate of NO (and NO_2) were calculated based on the equation as described in Schindlbacher et al. (2004).

In the year 2003, both, NO, NO_2 concentrations and O_3 concentrations (HORIBA APOA-360) were measured in the chamber atmosphere without using a filter. Nitric

oxide and NO_2 fluxes were calculated as described in Butterbach-Bahl et al. (1997), thus, taking the chemical reaction occurring between O_3 and NO in the chambers and in the tubing into account (Eq. 1).

$$F = \frac{Q \cdot (mNO_{mc} - mNO_{rc}) \cdot M_N \cdot 60 \cdot 10^6}{V_m \cdot A \cdot 10^9}$$

$$mNO_{mc} = k_3 \cdot mNO_t \cdot mO_{3t} \cdot t_{mc} + mNO_t$$

$$mNO_t = \frac{(mO_3 - mNO)mNO}{mO_3 \cdot 10^{(-k3\cdot(mO_3 - mNO)\cdot t_t)} - mNO}$$

$$mO_{3t} = \frac{(mNO - mO_3)mO_3}{mNO \cdot 10^{(-k3\cdot(mNO - mO_3)\cdot t_t)} - mO_3} \quad (1)$$

Where F is the flux rate [μg N m^{-2} h^{-1}], Q is the mass flow rate of air through the chamber (~0.001 m^3 min^{-1}), mNO_{mc}=corrected mixing ratio for NO in the measuring chamber [ppbv], mNO_{rc}=corrected mixing ratio of NO in the reference chamber, M_N is the atomic weight of N (=14.0067 g mol^{-1}), V_m is the standard gaseous molar volume (24.055 · 10^{-3} m^3 mol^{-1}), and A is the soil surface area of the chamber (0.0314 m^2), k_3=1,8 10^{-12} $e^{(1370/T)}$ [cm^3 $molecule^{-1}$ s^{-1}] or 4,8 10^{-2} $e^{(1370/T)}$ [$ppbv^{-1}$ min^{-1}], mNO_t=corrected mixing ratio for NO at the beginning of the tubing system [ppbv], mO_{3t}=corrected mixing ratio for O_3 at the beginning of the tubing system [ppbv], t_{mc} residence time of sample air in the measuring chamber [s], mNO=mixing ratio detected by the NO-analyzer [ppbv], mO_3=mixing ratio of O_3 detected by the O_3-analyzer [ppbv], T=temperature [K], t_t=residence time of sample air in the tubing [s].

NO_2 was calculated in analogy to NO flux rates (Butterbach-Bahl et al., 1997) using the NO_2-converter efficiency that was determined at the UBA, Vienna. It has to be mentioned that the NO_2 measurements with the HORIBA is the sum of NO_2 (most likely the main component) and other nitrogen compounds (PAN, NH_3, HONO).

In our calculations we have not considered for losses of NO, NO_2 or O_3 to the chamber walls, since a previous study by Ludwig (1994) showed that e.g. deposition of NO_x

to the chamber walls may in maximum contribute <20% to the total deposition flux even if the NO_x mixing ratio within the chamber was >15 ppbv. In view of the low concentrations and the spatial heterogeneity of NO_x fluxes the uncertainty coming from disregarding wall effects was therefore assumed to be of minor importance.

2.4. Soil samples

Around the chambers square plots of $4 \times 4\,m^2$ were marked. Every 2 months samples of the organic layer (frame 30×30 cm) and mineral soil cores (metal cylinder with 5 cm height, 6 cm diameter) were taken from the corners of each plot, moving clockwise in order to avoid re-sampling at the same spot. No soil samples were taken during snow cover. Four soil samples of each plot were pooled and sieved through a 2-mm sieve. Litter samples were pooled and ground. Soil and litter samples were analysed for extractable NH_4^+ and NO_3^- concentrations, soil moisture and pH. Ammonium and NO_3^- were extracted from soil with 0.1 M KCl. Ammonium was determined by a modified indophenol reaction (Kandeler, 1995). Nitrate was measured as NO_2^--N after reduction by copper sheathed zinc granulates. Values are reported in μg N g^{-1} soil dry weight (dw). Soil moisture was determined gravimetrically and the pH was measured in soil suspensions in 0.01 M $CaCl_2$ solution using a glass electrode.

2.5. Meteorological data

Air temperature (°C) and relative humidity (%) were measured with a combined temperature moisture sensor at 2 m above ground. Daily precipitation was taken from the nearest meteorological stations in Mariabrunn (2.7 km from SW) and from Alland (7 km from KL). Soil temperature was measured by thermocouples; and soil water content by a water content reflectometer (CS615) at a soil depth of 5 cm, 15 cm and 30 cm in SW and 15 cm, 30 cm and 60 cm in KL. Data were stored at an interval of 0.5 h in the data logger (Delta-T Logger).

2.6. Deposition measurements

Wet deposition was collected biweekly using 10 and 15 throughfall collectors, and 2 and 3 stemflow collectors for SW and KL, respectively. Litterfall was collected in three collectors. Wet deposition and litterfall was analysed for NH_4^+ and NO_3^-. Dry deposition of nitrogen dioxide (NO_2) and ammonia (NH_3) was captured by three passive diffusion tubes and three CEH ALPHA samplers (Tang, 2001) and were analysed by CEH Edinburgh. The samplers were placed at a height of 1.5 m in the canopy at the forest sites and at open sites nearby, and were changed monthly. In order to calculate the rates of dry deposition, deposition velocities of 1.5 mm s^{-1} for NO_2 and 3 mm s^{-1} for NH_3 (Duyzer, pers. comm.) were assumed.

2.7. Statistical analysis

Differences in soil emission, soil chemistry data and N-deposition data between the sites and between the investigation years were determined using the t-test or the non-parametric Wilcoxon-test. Prior to analysis the data were checked for normal distribution and for homogeneity of variances (t-test). When normal distribution could not be achieved by log-transformation the Wilcoxon-test was carried out. The relationships between daily, biweekly or monthly fluxes and soil, climate or deposition data were investigated using Pearson Correlation or Spearman rank correlation. As soil emissions, soil, and climate data were serially correlated over time, an autoregression procedure was used. The autoregression procedure provides regression models for time series data when the errors are autocorrelated or heteroscedastic. Data are said to be heteroscedastic (non-constant) if the variance of errors is not steady. As, one of the key assumptions of the simple linear regression model is that the errors have the same variance throughout a sample the regression model has to correct for heteroscedasticity. The generalized autoregressive conditional heteroscedasticity (GARCH) model was used to model and correct for heteroscedasticity. The GARCH (p, q) process assumes that the errors, although uncorrelated, are not independent and models the

time-varying conditional error variance as a function of the past realizations of the series (SAS/ETS, 1993). Models that take the changing variance into account can explore data more efficiently. The basic autoregressive conditional heteroscedasticity ARCH(q) model is the same as the GARCH(0,q) model, where (p) references about the number of autoregressive lags used and (q) references about the number of moving average lags are specified. The stepwise autoregressive error model was used for correcting autocorrelation. First, this method fits a high-order model with many autoregressive lags and then removes autoregressive parameters sequentially until all remaining autoregressive parameters display significant t-tests. With this model the most significant results can be detected. The basic equation for the autoregression model used is as follows (Eq. 2):

$$
\begin{aligned}
y_t &= \beta_0 + \beta_1 x_{1t} + \beta_2 x_{2t} + \ldots \beta_n x_{nt} + v_t \\
v_t &= \varepsilon_t - \varphi_1 v_{t-1} - \varphi_2 v_{t-2} - \ldots - \varphi_m v_{t-m} \\
\varepsilon_t &= \sqrt{h_t} e_t \\
h_t &= \omega + \sum_{i=1}^{q} \alpha_i \varepsilon_{t-i}^2 + \sum_{j=1}^{p} \gamma_j h_{t-j} \\
e_t &\sim IN(0, 1)
\end{aligned}
\tag{2}
$$

where y_t is the dependent variable for time t, β_0 is the intercept; $\beta_1, \beta_2, \ldots \beta_n$ are the regression coefficients of the independent variables (x_{it}, i=1 . . . n) where x_{1t} is soil moisture in 15 cm (SW) and 30 cm (KL) soil depth, x_{2t} is soil temperature in 3 cm (for N_2O), 5 cm (for NO) (SW) and 5 cm (KL) soil depth and x_{3t} is the CO_2 emission rate. v_t is the error term that is generated by the j^{th} order autoregressive process; φ_m are the autoregressive error model parameters (AR_m). The order of the process ($_m$) defines the number of past observations on which the current observation depends; ε_t is the unconditional variance and h_t is the GARCH (p, q) conditional variance; e_t is assumed to have a standard normal distribution; the parameters (ω and α_1) are ARCH

(q) model estimates and (γ_1) are GARCH (p) model estimates. Statistical analysis was either completed with SAS Enterpriseguide Version 2 or SAS Version 8. All differences reported were significant at $p<0.05$ unless otherwise stated.

3. Results

3.1. Meteorological data

The two years were characterized by extreme weather conditions. In summer/autumn 2002 disastrous flooding occurred all over Europe because of persistent rainfall followed by an extensive drought period in summer 2003. Consequently, the differences between the two seasons were pronounced, particularly in terms of soil moisture content. During both years significantly ($p<0.001$) lower mean soil moisture was recorded in SW (28% and 19%) in comparison to KL (42% and 37%). Mean annual air temperature was 8.0 and 8.2°C at SW and KL, respectively. In the second year higher mean annual air temperatures were recorded (8.6 and 8.8°C).

3.2. Soil nitrogen

At both sites NH_4^+ concentrations in mineral soil reached highest levels with concentrations of up to 17.3 μg NH_4^+-N g^{-1}dw in SW and 17.9 μg NH_4^+-N g^{-1} dw in KL in September 2002. In the first year mean NH_4^+-N concentrations were considerably higher compared to the quantified concentrations in the second year (Table 2), whereas NO_3^--N concentrations were higher in the second year. The soil in SW displayed highest NO_3^- concentrations in summer (max: 3.4 μg NO_3^--N g^{-1}dw) when *Allium* leaves had decayed completely and in autumn after litterfall (max: 2.3 μg NO_3^--N g^{-1} dw). The soil in KL showed highest NO_3^- concentrations from August to October 2003 (up to 1.3 μg N g^{-1}dw).

Total extractable soil N (NO_3^--N and NH_4^+-N) concentrations were found to be significantly ($p<0.001$) higher at both sites in the first year of investigation. Concentrations of available NO_3^- and NH_4^+ in the organic layer were about twice as large in soil samples from SW in comparison to KL but similar in terms of mineral soil (Fig. 2).

3.3. Nitrogen input

Nitrogen input by wet and dry deposition, litter decomposition and mineralized N are demonstrated in Table 2 and Fig. 3. Nitrogen input through litterfall to the forest floor amounted to 53–75 kg per ha^{-1} y^{-1} at SW, whereas in KL N-input through litterfall amounted to 59 kg per ha^{-1} y^{-1}.

Differences between the sites regarding the stem-flow of N were significant ($p<0.05$) in both years; differences in N from throughfall were significant in the second year. Dry deposition (NH_3, NO_2) was measured in the first year and amounted to a total of 2.38 and 0.85 kg ha^{-1} y^{-1} in SW and KL, respectively, thus, displaying highly significant differences between the sites ($p<0.001$). A total of 22.6 kg and 13.5 kg N ha^{-1} y^{-1} were deposited from the atmosphere in SW and KL, respectively (year 1). In the second year significantly lower rates of wet input were measured at both sites (Fig. 3).

3.4. Gas fluxes

3.4.1. CO_2 emissions

CO_2 fluxes are shown in Figs. 4a and 5a. The annual mean of CO_2 emissions varied between 33.0 and 43.4 mg CO_2-C m^{-2} h^{-1} at SW and between 29.2 and 31.6 mg CO_2-C $m^{-2}h^{-1}$ at KL, respectively (Table 3). Significant differences ($p<0.05$) between the sites were observed mainly during spring and autumn, whereas in summer and winter soil CO_2 fluxes did not differ remarkably between the sites. The fluxes showed clear seasonal variations which were strongly related to the air temperature. Maximum mean CO_2 fluxes were measured in summer 2002 (Figs. 4b, 5b). Lower emission

rates (<70 mg CO_2-C $m^{-2}h^{-1}$) were observed during the dry summer 2003. At SW a second emission peak could be observed in September, which is probably due to the decomposition of fresh litterfall. At both sites lowest CO_2 emission rates were measured in December; in SW 2.9±0.5 t C $ha^{-1}y^{-1}$ were emitted in the two years. In KL total gaseous C-losses from soil averaged 2.4 t C $ha^{-1}y^{-1}$ (Table 4). A correlation analysis showed that 76% and 89% of variances in CO_2 emissions at SW and KL could be explained by soil temperature ($p<0.001$). Furthermore, CO_2 emissions were negatively correlated with soil moisture in the upper 15 and 30 cm soil depth (SW: $r^2=-0.55$ and KL: $r^2=-0.40$).

3.4.2. N_2O emissions

At both sites N_2O emissions showed a comparable seasonal trend (Figs. 4b and 5b) with highest rates in summer and in late autumn.

At SW mean annual N_2O fluxes amounted to 10.4±0.6 µg N_2O-N m^{-2} h^{-1} in the first year of investigation. Maximum emissions occurred in July 2002 (75.4 µg N_2O-N m^{-2} h^{-1}) and minimum emission rates in winter 2002 (−6.3 µg N_2O-N m^{-2} h^{-1}). Nitrous oxide fluxes of up to 39 µg N_2O-N m^{-2} h^{-1} were observed during winter 2002 and reached almost the same magnitude as the peaks in spring and autumn. These high winter fluxes were observed during a period of warm weather and in connection with the thawing of the soil.

Nitrous oxide fluxes measured in KL were generally lower than those measured in SW (Table 5) except for measurements in April 2002 (39.2 µg N_2O-N m^{-2} h^{-1}), i.e. at the beginning of the measurements. This might be due to thinning of the stand in the previous winter. The annual mean N_2O flux was 6.8±0.5 µg N_2O-N m^{-2} h^{-1} in the first year with a minimum of −1.0 µg N_2O-N $m^{-2}h^{-1}$ in December and a maximum of 82.8 µg N_2O-N $m^{-2}h^{-1}$ in September. The mean annual N_2O emissions were higher in the second year (7.6±0.5 µg N_2O-N m^{-2} h^{-1}) (Table 3).

The variation coefficient between the manual chambers ranged from 20% to 180%

with highest variations in winter 2002 and in summer 2003.

Log-transformed N_2O emission rates measured by the manual chambers were positively correlated (SW: r^2=0.54, KL: r^2=0.56, p<0.001) with CO_2 emission rates and soil temperature (r^2=0.29, r^2=0.40, p<0.001). A significant positive dependency was found between soil N_2O emissions at SW and NO_3^--N concentrations in the organic layer (r^2=0.43, p<0.01), whereas N_2O emissions at SW were negatively correlated with soil moisture (r^2=−0.36, p<0.001) and precipitation (r^2=−0.34, p<0.001). There was no significant correlation between N_2O fluxes and soil moisture, precipitation or soil extractable N (NH_4^+ and NO_3^-) in KL.

Soil and meteorological parameters correlated with daily fluxes measured by AGPS as follows: Significant correlations (Pearson correlation coefficients) were detected between daily log-transformed N_2O and NO fluxes (r^2=0.23; p<0.001; n=289) in SW, while at KL a significant positive relationship with soil temperature (p<0.01; r^2=0.16; n=330) and a negative relationship with soil moisture (p<0.01; r^2=−0.15; n=330) was demonstrated.

A GARCH (1,1) model was developed to predict mean log-transformed N_2O emissions from soil, in SW (Model 1; r^2=0.53) and in KL (Model 2; r^2=0.73) (Figs. 6a, 6b). Estimated parameters are shown in Table 6. Due to the fact, that the correlation analysis revealed significant effects of soil moisture (in 15 cm, 30 cm soil depth, respectively), soil temperature (3 cm) and CO_2 emission rates at our sites these variables were used within the GARCH model. Furthermore these variables were measured regularly and simultaneously with N_2O emissions from the manual chambers. For model 1 soil temperature was squared for removing negative values. For model 2 (KL) mean CO_2 emissions (x_3) were log–transformed. By applying the GARCH (1, 1) model and hence the calculation of an autoregressive error term, significant effects of variables could be detected that had not been visible before (Table 6).

3.4.3. NO_x emissions

In SW the fluxes from soil of NO_x were measured from June 2002 until May 2004 (Fig. 7a). During winter no flux measurements were carried out. Mean NO emission rates were 3.6±0.1 μg NO-N m^{-2} h^{-1} in the first year (June–November 2002; n=114) with no significant differences between monthly means. In the second year (May 2003–January 2004; n=195) significantly higher emission rates were measured with a mean of 7.4±0.6 μg NO-N m^{-2} h^{-1} (Table 3). Highest NO emissions were measured in September after a rainfall event (35 mm), which occurred after an extended dry period at low soil moisture contents (7–17%) and at soil temperatures between 10 and 15°C. Nitrogen dioxide was permanently deposited throughout the entire observation period with a mean of −2.7±0.09 μg NO_2–N m^{-2} h^{-1} (n=280). Only in July the soil seemed to act as a weak net source of NO_2.

To quantify soil NO_x fluxes at KL measuring campaigns were carried out between August and October 2003. The mean NO fluxes measured in this period were 0.7±0.1 μg NO-N m^{-2} h^{-1} in KL, whereas for the same period of time, significantly ($p<0.001$) higher fluxes (Fig. 7b) with a mean of 10.4±1.3 μg NO-N m^{-2} h^{-1} (−0.8 to 44.9 μg N $m^{-2}h^{-1}$) were detected at SW. At KL a weaker deposition of NO_2 was observed with a mean of −0.6±0.06 μg NO_2–N $m^{-2}h^{-1}$.

At SW mean daily NO fluxes were negatively correlated with soil moisture measured in a soil depth of 5 cm and 15 cm ($r^2=-0.43$, $p<0.001$, n=302). Daily variations in NO emission could partly be explained by changes in soil temperature at a depth of 5–30 cm ($r^2=0.23$, $p<0.001$), and by air temperature ($r^2=0.17$, $p<0.01$), respectively. NO and N_2O emissions were positively correlated ($r^2=0.23$, $p<0.001$) in SW. A simple regression model could not be developed to identify relationships between NO emissions and other parameters because residuals were correlated over time. An autoregression model (Model 3) was developed, where soil moisture at 15 cm soil depth (x_{1t}) and soil temperature at 5 cm soil depth (x_{2t}), describes daily mean NO emission with a total r^2 of 0.95 (Fig. 7). The model revealed a time-lag of 14, which means that actual NO

emissions reflect changes in soil moisture and soil temperature over a period of 14 days. Regression parameters demonstrate the negative effect of soil moisture (β_1) and the positive effect of soil temperature (β_2) (Table 6).

At KL, NO emissions showed a significant positive correlation with soil (r^2=0.44, p<0.001, n=66) and air temperature (r^2=0.66 p<0.001), but NO fluxes were negatively correlated with soil moisture (r^2=−0.32, p<0.01). There was no significant correlation between NO and N_2O emissions in KL (r^2=0.29, p=0.06). Nitric oxide emissions in KL could be predicted by soil moisture at a soil depth of 30 cm (x_{1t}) and through soil temperature in 5 cm soil depth (x_{2t}) with a total r^2 of 0.73 (Model 4). Expressing the prediction of NO emissions of both sites through one model (Model 5) resulted in a 5^{th} order autoregressive model (lag of 5 days) with a total r^2 of 0.85 (Model 5). Soil moisture was the most significant (p<0.001) parameter. Soil temperature was significant at p<0.01. Estimated parameters for the models are shown in Table 6.

3.4.4. Effects of N-input on gaseous N-losses

To identify if N-input affects the gaseous N-losses on longer time scales monthly mean N deposition rates were smoothed by using a moving average of 2 or 3. The correlation coefficients of the mean N_2O and NO monthly emission rates measured in SW and KL and N-deposition values are outlined in Table 7. The correlation between N input and N trace gas emissions were found to be closer for KL, i.e. the less N saturated site. Correlations between N input and mean N_2O emissions were especially pronounced as calculated from daily measurements. In KL highly significant correlations between N_2O emissions and deposited NO_3^- and NH_4^+ via stemflow were found. In addition, a significant correlation could be demonstrated for NH_4^+ entering the ecosystem via throughfall. In SW a significant relationship between N_2O emissions and atmospheric N-deposition could only be demonstrated for dry deposition and NH_4^+ originating from wet (throughfall and stemflow) deposition (Table 7). Furthermore, close correlations were observed between NO emissions, dry NO_2 deposition and wet NH_4^+ deposition.

No correlation existed between NO emission and NO_3^- deposition. Due to the short period of time regarding the measurements of NO at KL (3 months) we could not produce the same statistical analysis for this site.

4. Discussion

4.1. CO_2 emissions

At our sites, between 70–90% of the temporal variations of soil respiration could be explained by soil temperature. The highest CO_2 emissions were detected in spring 2002, when the increase of soil temperature and the mineralization of the litter led to a peak in CO_2 emissions. Zechmeister-Boltenstern et al. (2002) found that in SW, CO_2 emission always peaked in late spring due to the fast decomposition of *Allium* leaves, which cover the ground only from April to June.

Another important variable affecting respiration rates is soil water content. Low CO_2 emissions are often observed when soils are either waterlogged or dry (Ball et al., 1999; Lee et al., 2002; Howard and Howard, 1993; Smith et al., 2003). In 2003 a continuous decrease of soil moisture was observed: from 22% at the end of May to 8% at early September. This explains why CO_2 emissions measured in the summer months of 2003 were significantly lower as compared to emissions measured in summer 2002. In both years and at both sites lowest emission rates were measured at the beginning of the vegetation period as a result of low temperatures and, subsequently, lower activity of heterotrophic microorganisms and root respiration. The overall negative relationship between soil CO_2 emissions and soil water content are due to low CO_2 emissions in winter during periods of high soil water content. The cumulative CO_2 losses (2.3–2.9 t C ha^{-1} y^{-1}) from the sites (Table 4) are in good agreement with annual CO_2 fluxes from temperate, broad-leaved and mixed forest soils as reported by (Raich and Schlesinger, 1992).

4.2. N_2O emissions

During the two years of measurements N_2O emissions followed a similar seasonal trend as observed at these sites in earlier years by Meger (1997), Hahn et al. (2000) and Zechmeister-Boltenstern et al. (2002). Highest N_2O emissions in SW were measured in June 2002 when soils were moist and soil temperatures were high. Schindlbacher et al. (2004) found maximum N_2O emissions at a soil temperature of 20°C and at a water-filled pore space (WFPS) of 85–95% in laboratory studies with soils from both sites. The reported percentage of WFPS corresponds with a soil moisture content of 50–56% in SW and 56–63% in KL. As the soil in SW never reached the moisture optima, significantly higher N_2O emissions can be expected in the case of high soil moisture content. The overall negative correlation between soil N_2O emissions and soil water content are due to low emissions in winter during periods of high soil water content. During the vegetation period a positive dependency is found.

In SW the decomposition of decaying *Allium* leaves led to high N mineralization rates in early summer (Zechmeister-Boltenstern et al., 2002). The mineralized N was immediately transformed during nitrification and denitrification resulting in high N_2O emissions.

The meteorological conditions of the two experimental years were highly different in terms of the occurrence of dry periods of temperature maxima, thus causing pronounced interannual variations. The year 2002 was characterized by a very wet summer. In contrast meteorological conditions observed in summer 2003 showed significantly lower precipitation and higher temperatures: The mean soil moisture was about 10% lower and mean soil temperature about 0.6°C higher. The impact of drought in 2003 was even more pronounced at SW. During summer soil microbial activity, especially the activity of anaerobic denitrifying bacteria is strongly related to water availability (Schürmann et al., 2002). When soil desiccates, microbial activity is inhibited. High emissions were measured during the first rain after drought. In September 2003, when soil moisture increased from 9% to 12% during a precipitation event of 35 mm rainfall,

a sudden increase in N_2O emissions was observed. Microorganisms in the very dry soil produced high emissions after this rainfall event. Comparable results of re-wetting of dry temperate forest soils on N_2O emissions were also observed by Brumme et al. (1999).

In the soil at SW the concentration of NO_3^- is higher as compared to the soil NO_3^- concentrations in KL or other soils in the region (Zechmeister-Boltenstern et al., 2002; Hackl et al., 2004); therefore nitrification might play an important role in the production of N_2O at SW. Both investigation years were characterized by a dry and warm spring. As nitrification is strongly dependent on the O_2 concentration in the soil and on soil temperature we hypothesize that, especially in spring, nitrification was the main source of N_2O production.

Generally, lowest emissions were detected in winter. However, some high winter N_2O fluxes of up to 39 μg N_2O-N m^{-1} h^{-1} were found after freezing and thawing events. The winter fluxes account for 16%–32% of the total annual emissions.

Total annual N_2O emissions at SW were in the range of 0.65 and 0.77 kg N_2O-N ha^{-1} y^{-1} (Table 4). At the low N-input site KL annual N_2O emissions were significantly lower (0.51 and 0.52 kg N_2O-N ha^{-1} y^{-1}). The calculated annual N_2O emission rates at both sites are still to some extent uncertain since e.g. in our measurements diurnal variations are not included and the location of our plots was in interstem areas which might lead to underestimations (Butterbach-Bahl et al., 2002b). Annual N_2O emissions at SW and KL were within the same range as reported for other temperate deciduous forests, which have been shown to vary from 0 to 10 kg N ha^{-1} (Brumme and Beese, 1992; Wolf and Brumme, 2003; Brumme et al., 1999; Oura et al., 2001; Papen and Butterbach-Bahl, 1999). In a Danish beech forest (N-input: 25.6 kg N ha^{-1} y^{-1}) N_2O emissions were estimated to be 0.5 kg N ha^{-1} y^{-1} (Beier et al., 2001).

4.2.1. N_2O emissions and N-deposition

The main question of our project was, whether nitrogen deposition can have an effect on N_2O emissions (Brumme et al., 1999). Some studies suggest that forests receiving high N-deposition are emitting higher rates of N_2O than forests exposed to low N-deposition (Castro et al., 1993; Butterbach-Bahl et al., 1997, 2002a). As a consequence of lower precipitation rates wet N-input was lower at both sites in the year 2003 as compared to the year 2002. Nitrous oxide emissions were found to be significantly correlated with precipitation and N-input. In our study N_2O emissions measured with high time-resolution showed a closer relationship to N-deposition than measurements with high spatial resolution. At the low N-input site KL, higher and stronger correlations between N_2O emissions and N-deposition were observed in comparison to the high N-input site SW (Table 7). These results indicate that low N-deposition sites seem to be more responsive to N-deposition events than forest sites receiving chronically high rates of N deposition.

4.3. NO emissions

At SW total NO emissions in the investigation period were 0.2 and 0.7 kg N ha^{-1} (Table 4). This considerable interannual variation was mainly caused by the extremely contrasting weather conditions during the two years. Soil moisture, followed by soil temperature, were the most important factors affecting the magnitude of soil NO emissions. NO emissions were found to be highest at intermediate soil water contents (van Dijk et al., 2002). Under waterlogged conditions NO can easily be reduced to N_2O or N_2 before the N may escape to the atmosphere (Venterea and Rolston, 2000; Davidson et al., 2000). On the other hand, NO emission can also be low, when dry soil conditions constrain microbial activity (Galbally, 1989; Ludwig et al., 2001). In laboratory studies (Schindlbacher et al., 2004) maximum NO emissions occurred at a soil temperature of 20°C and a WFPS of 30–45% at SW and 65% at KL. These values correspond to a soil moisture content of 18–26% and 43% and are in good agreement with the en-

vironmental conditions at periods with highest NO emissions as observed by the field measurements. In our study NO emissions were negatively correlated with soil moisture at both sites. Rain induced pulses in NO emissions as observed at our sites in September 2003 have also been observed in seasonally dry ecosystems (Davidson, 1992; Otter et al., 1999). At SW a pulse of NO emissions, amounting to almost 50% of the annual emission, was recorded when soil was moistened after a long dry period, caused by a rainfall event (<35 mm). The effect of rain on dry soils may lead to a sudden burst of mineralization and nitrification (Schmidt, 1982; Davidson et al., 1991; Williams et al., 1992). This increase of NO emissions can last several days after the water addition (Anderson and Levene, 1987; Slemr and Seiler, 1984). At both sites NO_2 was deposited. Mean daily NO_2 deposition was $-42.6\,\mu g\ NO_2\text{-N}\ m^{-2}\ h^{-1}$ and $-2.9\,\mu g\ NO_2\text{-N}\ m^{-2}\ h^{-1}$ in SW and $-0.64\,\mu g\ NO_2\text{-N}\ m^{-2}\ h^{-1}$ in KL. Only once we observed a weak net emission of NO_2 from the soil at the SW site and that was in July 2003. As our NO_x analyzer doesn't measure NO_2 specifically, the upward flux of NO_2 could be explained by the conversion of HONO, which might be abundant in substantial amounts in forest atmospheres (Kleffmann et al., 2005). It has to be mentioned that NO_x and O_3 was measured in year 2003, but not in year 2002 where we used a filter to remove air impurities.We couldn't compare the differences in NO emissions between the two years regarding the different methods.

4.3.1. NO emissions and N-deposition

Mean monthly NO fluxes from the soil in SW ranged between 2.1 and 21.2 μg NO-N $m^{-2}\ h^{-1}$ and were, thus significantly ($p<0.001$) higher than those measured from KL. The NO emission rates at the site SW were higher than the values of a deciduous forest ecosystem (oak-hickory: 0.2–4 μg NO-N $m^{-2}\ h^{-1}$) reported by Williams and Fehsenfeld (1991) and within – or slightly lower – than reported NO emissions for the Höglwald beech site in Germany (6.1–47 μg NO-N $m^{-2}\ h^{-1}$) (Butterbach-Bahl et al., 1997) and for a beech forest at Sorø, Denmark (<1 kg $NO_x\ ha^{-1}\ y^{-1}$) (Beier et al., 2001). At KL

0.02 kg NO-N ha^{-1} were emitted from soil from August to October 2003. The soil in SW received 70% more N from the atmosphere and 16 times more NO was produced (0.32 kg N ha^{-1}). These data support the close relationship between atmospheric N-deposition and NO flux rates.

4.4. Time series analysis

As N_2O and NO emission data were autocorrelated over time, time series analysis were conducted to predict N_2O and NO emissions from our sites taking time deferred relationships into account. Through the autoregression models the temporal variation of NO and N_2O emissions could be explained by soil moisture, soil temperature as well as CO_2 emission as an indicator of general microbial activity. The results of GARCH modelling for N_2O emissions of the individual sites depicted better predicted values (SW: r^2=0.53 and KL: r^2=0.73) compared to a simple regression model (SW: r^2=0.28 and KL: r^2=0.46).

Temporal variations in NO emissions could hardly be explained by a simple regression model using soil moisture and soil temperature as drivers (SW: 18% KL: 39%). However, when taking previously measured (daily mean) soil moisture and soil temperature into account up to 95% and 73% of the variations of NO emission could be explained in SW and KL, respectively. Simulation results were at their best for the year 2002, when spatial variations were small due to continuously high soil moisture. As a result of soil desiccation in summer 2003 spatial variation was higher and the fit between simulated and measured values was lower. It is said that through individual measurements of soil moisture and soil temperature in each chamber even better predictions of emissions could be achieved.

Modelled annual NO emissions for SW amounted to 0.18 and 0.39 kg NO-N ha^{-1} y^{-1} for the two years of investigation (Table 4). Using values of mean soil moisture and soil temperature measured daily over a period of two investigation years in order to drive the empirical model, we estimated annual NO-losses at KL to be in the range of 0.02

and 0.03 kg NO-N ha^{-1} y^{-1} (Table 4).

5. Conclusions

Our results show that the temporal pattern of CO_2 and N-oxides emissions is strongly dependent on temperature. However, short-term fluctuations in N trace gas emissions can also be modulated by changes in soil moisture or freezing-thawing events. In our study significant interannual variations in the magnitude and seasonality of N trace gas emissions were demonstrated at both forest sites. Therefore, long-term measurements on a larger scale covering several years – as suggested by Ambus and Christensen (1995) – are needed to finally come up with reliable estimates of forest soil emissions.

Since in our study we found a detectable effect of topographic structures on N_2O fluxes, we hypothesize that medium scale measurements in the range of several 100 m would increase the accuracy of nitrous oxide emission estimates from forests. Thus, variability caused by topographic structures could be detected.

Nitrogen-input had a strong impact on N-emissions at our sites. Nitric oxide emissions from the soil were stronger affected by atmospheric N-deposition than N_2O emission. The temporal relationship between N-inputs and N-emissions was stronger for the N-limited forest ecosystem suggesting that – under increased N-input – such ecosystems can potentially function as strong sources of N trace gases if in the future.

Emission data were autocorrelated over time. Therefore time series analysis was used which revealed patterns that did not become apparent through simple regression models. Nitrogen oxide emissions from soils could be predicted with a higher r^2. Since there are few studies in soil science which apply more complex models rather than simple regression analysis, we would like to emphasize the potential of such models for data analysis and the prediction of GHG-emissions.

Acknowledgements. We would like to thank the forest managers S. Jeitler and J. Wimmer for giving access to their properties. A. Fiege, F. Winter for field works and C. Abo-Elschabaik and

M. Kitzler for helping with the sample analysis, S. Wolf for English corrections and K. Gartner for provision of meteorological data. The authors also thank K. Moder, T. Gschwantner for their constructive work with statistics and R. Jandl and A. Schindlbacher for comments and discussion. The study is a part of the NOFRETETE project EVK2-CT2001-00106 funded by the European Commission DG Research – Vth Framework Programme.

References

Aber, J., McDowell, W., Nadelhoffer, K., Magill, A., Berntson, G., Kamakea, M., McNulty, S., Currie, W., Rustad L., and Fernandez I.: Nitrogen saturation in temperate forest ecosystems, Bioscience, 48, 11, 921–934, 1998.

Ambus, P. and Christensen, S.: Spatial and seasonal nitrous oxide and methane fluxes in Danish forest-, grassland-, and agroecosystems., J. Environ. Qual., 24, 993–1001, 1995.

Anderson, I. C. and Levene, J. S.: Simultaneous field measurements of nitric oxide and nitrous oxide, J. Geophys. Res., 92, 964–976, 1987.

Ball, B. C., Scott, A., and Parker, J. P.: Field N_2O, CO_2 and CH_4 fluxes in relation to tillage, compaction and soil quality in Scotland, Soil Till. Res., 53, 29–39, 1999.

Beier, C., Rasmussen, L., Pilegaard, K., Ambus, P., Mikkelsen, T., Jensen, N. O., Kjøller, A., Priemé, A., and Ladekarl, U. L.: Fluxes of NO_3^-, NH_4^+, NO, NO_2, and N_2O in an old Danish beech forest, Water, Air and Soil Pollution: Focus, 1, 187–195, 2001.

Brumme, R. and Beese, F.: Effects of liming and nitrogen fertilization on emissions of CO_2 and N_2O from temperate forest, J. Geophys. Res., 97, 12, 851–858, 1992.

Brumme, R., Borken, W., and Finke, S.: Hierachical control on nitrous oxide emission in forest ecosystems, Global Biogeochem. Cycles, 13, 1137–1148, 1999.

Butterbach-Bahl, K., Gasche, R., Breuer, L., and Papen, H.: Fluxes of NO and N_2O from temperate forest soils: impact of forest type, N-deposition and of liming on NO and N_2O emissions, Nutr. Cycl. Agroecosyst., 48, 79–90, 1997.

Butterbach-Bahl, K., Gasche, R., Huber, C., Kreutzer, K., and Papen, H.: Impact of N-input by wet depostion on N-trace gas fluxes and CH_4-oxidation in spruce forest ecosystems of the temperate zone in Europe, Atmos. Environ., 32, 3, 559–564, 1998.

Butterbach-Bahl, K., Breuer, L., Gasche, R., Willibald, G., and Papen, H.: Exchange of trace gases between soils and the atmosphere in Scots pine forest ecosystems of the North East-

ern German Lowlands, 1. Fluxes of N_2O, NO/NO_2 and CH_4 at forest sites with different N-deposition, Forest Ecology and Management, 167, 123–134, 2002a.
Butterbach-Bahl, K., Rothe, A., and Papen, H.: Effect of tree distance on N_2O and CH_4-fluxes from soils in temperate forest ecosystems. Plant and soil, 240, 91–103, 2002b.
Castro, M. S., Steudler, P. A., Melillo, J. M., Aber, J. D., and Millham, S.: Exchange of N_2O and CH_4 between the atmosphere and soils in spruce-fir forests in the north-eastern United States, Biogeochemistry, 18, 119–135, 1993.
Dahlgren, R. A. and Singer, M. J.: Nutrient cycling in managed and non-managed oak woodland-grass ecosystems, University of California, Davis, CA, 1994.
Davidson, E. A., Vitousek, P. M., Matson, P. A., Riley, R., Garcia-Mendez, G., and Maass, J. M.: Soil emissions of nitric oxide in a seasonally dry tropical forest of Mexico, J. Geophys. Res., 96, 15 439–15 445, 1991.
Davidson, E.: Pulses of nitric oxide and nitrous oxide flux following wetting of dry soil: an assessment of probable sources and importance relative to annual fluxes, Ecological Bulletins, 42, 149–155, 1992.
Davidson, E. A.: Soil water content and the ratio of nitrous oxide to nitric oxide emitted from soil, in: Biogeochemistry of global change, edited by: Oremland, R. S. , Chapman and Hall, New York, 369–386, 1993.
Davidson, E. A. and Kingerlee, W.: A global inventory of nitric oxide emissions from soils, Nut. Cycling Agroecosys., 48, 37–50, 1997.
Davidson, E. A., Keller, M., Erickson, H. E., Verchot, L. V., and Veldkamp, E.: Testing a conceptual model of soil emissions of nitrous and nitric oxides, BioScience, 50, 667–680, 2000.
Fitzhugh, R. D., Driscoll, C. T., Groffman, P. M., Tierney, G. L., Fahey, T. J., and Hardy, J. P.: Effects of soil freezing disturbance on soil solution nitrogen, phosphorus and carbon chemistry in a northern hardwood ecosystem, Biogeochemistry, 56, 215–238, 2001.
Galbally, I. E.: Factors controlling NO_x emissions from soil, in: Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, edited by: Andreae, M.O. and Schimel, D.S., John Wiley, New York, 23–37, 1989.
Galloway, J. N., Schlesinger, W. H., II, H. L., Michaels, A., and Schnorr, J. L.: Nitrogen fixation: anthropogenic enhancement-environmental response, Global Biogeochem. Cycles, 9, 2, 235–252, 1995.
Gundersen, P., Emmett, B. A., and Konaas, O. J.: Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis on NITREX data, Forest Ecology and Management, 101, 37–

55, 1998.
Hackl, E., Bachmann, G., and Zechmeister-Boltenstern, S.: Microbial nitrogen turnover in soils under different types of natural forest, Forest Ecology and Management, 188, 101–112, 2004.
Hahn, M., Gartner, K., and Zechmeister-Boltenstern, S.: Greenhouse gas emissions (N_2O, CO_2 and CH_4) from beech forests near Vienna with different water and nitrogen regimes, Die Bodenkultur – Austrian Journal of Agricultural Research, 51, 91–101, 2000.
Hall, S. J. and Matson, P. A.: Nitrogen oxide emissions after nitrogen additions in tropical forests, Nature, 400, 152–155, 1999.
Holtermann, C.: A transportable system for the on-line-measurement of NO_x (NO, NO_2) emission from soils, Die Bodenkultur, 47, 235–244, 1996.
Howard, D. M. and Howard, P. J.: Relationships between CO_2 evolution, moisture content and temperature for a range of soil types, Soil Biology & Biochemistry, 25, 1537–1546, 1993.
IAEA: Manual on measurements of methane and nitrous oxide emissions from agriculture. International Atomic Energy Agency, Vienna, 90, 1992.
Kandeler, E.: Ammonium and Nitrate, in: Methods of Soil Biology, edited by: Schinner, F., Öhlinger, T., Kandeler, E., and Margesin, R., Springer, Berlin, 406–410, 1995.
Kleffmann, J. Gaviloaiei, T., Hofzumahaus, A., Holland, F., Koppmann, R., Rupp, L., Schlosser, E., Siese, M., and Wahner, A.: Daytime formation of nitrous acid: A major source of OH radicals in a forest, Geophys. Res. Lett., 32, L05818, doi:10.1029/2005GL022524, 1–4, 2005.
Lee, M. S., Nakane, K., Nakatsubo, T., Mo, W. H. and Koizumi, H.: Effects of rainfall events on soil CO_2 flux in a cool temperate deciduous broad-leave forest, Ecol. Res., 17, 401–409, 2002.
Lovett, G. M., Weathers, K. C., and Arthur, M. A.: Control of nitrogen loss from forested watersheds by soil carbon: Nitrogen ratio and tree species composition, Ecosys., 5, 712–718, 2002.
Ludwig, J.: Untersuchungen zum Austausch von NO und NO_2 zwischen Atmosphäre und Biosphäre, PhD Thesis, University of Bayreuth, 251 pp., 1994.
Ludwig, J., Meixner, F. X., Vogel, B., and Förstner, J.: Processes, influencing factors, and modelling of nitric oxide surface exchange – an overview, Biogeochemistry, 52, 3, 225–257, 2001.
MacDonald, J. A, Dise, N. B., Matzner, E., Armbruster, M., Gundersen, P., Forsius, M.: Nitrogen input together with ecosystem nitrogen enrichment predict nitrate leaching from European

forests, Global Change Biology, 8, 1028–1033, 2002.
Mayer, H.: Wälder des Ostalpenraumes, Fischer Verlag, 344, 1974.
Meger, S.: Sticksoffkreislauf und Methanoxidation in Buchenwälder, University Vienna, Vienna, 106, 1997.
NADP: National Atmospheric Deposition Program 2001 Summary. NADP Report, http://nadp.sws.uiuc.edu/lib/data/2001as.pdf, Illinois State Water Survey, Champaign, IL, 2002.
Otter, L., Yang, W., Scholes, M. and Meixner, F. X.: Nitric oxide emissions from a southern African savanna. J. Geophys. Res.-A., 104 (D15), 18 471–18 485, 1999.
Oura, N., Shindo, J., Fumoto, F., Toda, H., and Kawashima, H.: Effects of nitrogen deposition on nitrous oxide emissions from the forest floor, Water, Air and Soil Pollution, 130, 673–678, 2001.
Papen, H. and Butterbach-Bahl, K.: A 3-year continuous record of nitrogen trace gas fluxes from untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany, 1. N_2O emissions, J. Geophys. Res. 104, 18 487–18 503, 1999.
Pilegaard, K., Hummelshoj, P., and Jensen, N. O.: Nitric oxide emission from a Norway spruce forest floor, J. Geophys. Res., 104, 3433–3445, 1999.
Raich, J. W. and Schlesinger, W. H.: The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate, Tellus, 44B, 81–99, 1992.
Rennenberg, H., Kreutzer, K., Papen, H., and Weber, P.: Consequences of high loads of nitrogen for spruce (*Picea abies*) and beech (*Fagus sylvatica*) forests, New Phytol, 139, 1, 71–86, 1998.
SAS/ETS: User's Guide. Version 8. Cary: Statistical Analysus System Institute, 1993.
Schindlbacher, A., Zechmeister-Boltenstern, S., and Butterbach-Bahl, K.: Effects of soil moisture and temperature on NO, NO_2 and N_2O emissions from forest soils, J. Geophys. Res., 109, D17302, 1–12, 2004.
Schmidt, E. L.: Nitrification in soil, in: Nitrogen in agricultural soils, edited by: Stevenson, F .J., Agron. Monogr. 22, ASA, CSSA, and SSSA. Madison, WI, 253–288, 1982.
Schürmann, A., Mohn, J., and Bachofen, R.: N_2O emissions from snow-covered soils in the Swiss alps, Tellus B, 54, 2, 134–142, 2002.
Skiba, U. M., Sheppard, L. J., MacDonald, J., and Fowler, D.: Some key environmental variables controlling nitrous oxide emissions from agricultural and semi-natural soils in Scotland, Atmospheric Environment, 32, 3311–3320, 1998.
Skiba, U., Sheppard, L. J., Pitcairn, C. E. R., VanDijk, S., and Rosall, M. J.: The effect of N-

deposition on nitrous oxide and nitric oxide emissions from temperate forest soils, Water, Air and Soil Pollution, 116, 89–98, 1999.
Slemr, F. and Seiler, W.: Field Measurements of NO and NO_2 Emissions from Fertilized and Unfertilized Soils, J. Atmos. Chem., 2, 1–24, 1984.
Smith, K. A. Ball, T., Conen, F., Dobbie, D. E., Massheder, J., and Rey, A.: Exchange of greenhouse gases between soil and atmosphere: Interactions of soil physical factors and biological processes, Eur. J. Soil Science, 54, 4, 779–791, 2003.
Tang, Y. S., Cape, J. N., and Sutton, M. A.: Development and types of passive samplers for monitoring atmospheric NO_2 and NH_3 concentrations, The Scientific World, 1, 513–529, 2001.
Tietema, A.: Mass loss and nitrogen dynamics in decomposing acid forest litter in the Netherlands at increased nitrogen deposition, Biogeochemistry, 20, 45–62, 1993.
Van Breemen, N., Burrough, P. A., Velthorst, E. J., van Dobben, H. F., de Wit, T., Ridder, T. B., and Reijnders H. F. R.: Soil acidification from atmospheric ammonium sulphate in forest canopy throughfall, Nature, 299, 548–550, 1988.
Van Dijk, S. M., Gut, A., Kirkman, G. A., Meixner, F. X., and Andreae, M. O.: Biogenic NO emissions from forest and pasture soils: Relating laboratory to field measurements, J. Geophys. Res., 107, D20:8058, 2002.
Venterea, R. T. and Rolston, D. E.: Mechanisms and kinetics of nitric and nitrous oxide production during nitrification in agricultural soil, Global Change Biology, 6, 303–316, 2000.
Venterea, R. T., Groffman, P. M, Verchot, L. V., Magill, A. H., Aber, J. D., and Steudler, P. A.: Nitrogen oxide gas emissions from temperate forest soils receiving long-term nitrogen inputs, Global Change Biology, 9, 346–357, 2003.
Williams, E. J. and Fehsenfeld, F. C.: Measurement of soil nitrogen oxide emissions at three North American ecosystems, J. Geophys. Res., 96, 1033–1042, 1991.
Williams, E. J., Hutchinson, G. L., and Fehsenfeld, F. C.: NO_x and N_2O emissions from soil, Global Biogeochem. Cycles, 6, 351–388, 1992.
Wolf, I. and Brumme, R.: Dinitrogen and nitrous oxide formation in beech forest floor and mineral soils, Soil Sci. Soc. Amer. J., 67, 1862–1868, 2003.
Zechmeister-Boltenstern, S., Hahn, M., Meger, S. and Jandl, R.: Nitrous oxide emissions and nitrate leaching in relation to microbial biomass dynamics in a beech forest soil, Soil Biol Biochem, 34, 823–832, 2002.

Table 1. Site and soil characteristics of the sites SW and KL.

	SW	KL
Location	48°14´N 16°15´E	48°07´N 16°03´E
Precipitation [mm]	465[1)]	728[1)]
Mean air temp. [°C]	9	8
Vegetation	*Lathyro-Fagetum Allietosum*[2)]	*Asperulo odoratae-Fagetum*[2)]
Stand age [years]	142	62
Exposition, elevation	SE, 370 m a sl.	NNE, 510 m a sl.
Tree height [m]	33.0	25.1
DBH [cm]	51.0	21.8
Basal area [m^2 ha^{-1}]	40.0	25.6
Soil type	dystric cambisol over sandstone	
Water conditions	moderately well-drained	moderately fresh
Soil texture	silty loam	loam-loamy clay
Soil pH 0-7cm ($CaCl_2$)	4.4	4.6
C:N	16	16
Soil density (g cm^{-3})	0.630	0.827
N_{tot} (mg g^{-1})	2.38	4.79
C_{org} (mg g^{-1})	37.70	74.51

[1)] Mean precipitation of the two observation years. [2)] (Mayer, 1974).

Table 2. Wet and dry deposition, precipitation, litter-fall, soil nitrogen and pH ($CaCl_2$) in year 1 (May/02–April/03) and year 2 (May/03–April/04) at the two investigation sites.

		SW				KL			
		year 1		year 2		year 1		year 2	
N-input by wet deposition [kg ha^{-1} y^{-1}]									
throughfall	NH_4^+	8.6		4.8		5.5		2.5	
	NO_3^-	7.7		9.9		6.0		2.5	
stemflow	NH_4^+	2.7		2.6		0.6		0.4	
	NO_3^-	1.2		2.1		0.5		0.3	
Sum of wet deposition		**20.2**		**19.4**		**12.6**		**5.7**	
N-input by dry deposition [kg ha^{-1} y^{-1}]									
	NH_3	1.08		n.m.		0.23		n.m.	
	NO_2	1.30		n.m.		0.62		n.m.	
Sum of dry deposition		**2.38**		**n.m.**		**0.85**		**n.m.**	
Precipitation [mm]		530		400		765		690	
Litter-fall [kg dw ha^{-1} y^{-1}]		4030 (177)		5963 (920)		6840		n.m.	
N - litterfall [kg N ha^{-1} y^{-1}]		52.8 (3.7)		74.5 (10.6)		59.2		n.m.	
Organic layer [µg N g^{-1} dw]	NH_4^+	97.6 (9.4)	**	55.0 (5.6)	**	50.0 (4.3)		25.5 (1.5)	
	NO_3^-	19.5 (1.8)	**	27.5 (2.8)	*	11.4 (1.2)		18.0 (2.3)	
pH ($CaCl_2$)		5.7 (0.1)	*	5.7 (0.1)	*	5.4 (0.1)		5.2 (0.1)	
Mineral soil [µg N g^{-1} dw]	NH_4^+	9.4 (1.4)	*	4.0 (0.4)		11.5 (1)	*	5.7 (0.5)	
	NO_3^-	1.5 (0.3)	***	1.7 (0.2)	*	0.4 (0.1)		0.9 (0.1)	
pH ($CaCl_2$)		4.4 (0.1)		4.3 (0.04)		4.6 (0.1)		4.6)	

Note: Deposition data and precipitation are sums. Soil data are means with standard error in parenthesis. [1)] Starting from August 2002. Asterisk indicate significant differences between the sites for the individual years (* $p<0.05$, **$p<0.01$, ***$p<0.001$). n.m. = not measured.

Table 3. Mean annual CO_2-C [mg C $m^{-2}h^{-1}$], N_2O-N and NO-N [μg N $m^{-2}h^{-1}$] losses±S. E at SW and KL in the two investigation years. Minimum and maximum values are in parenthesis.

	SW			KL		
	CO_2	N_2O	NO	CO_2	N_2O	NO
	[mg C m^{-2} h^{-1}]	[µg N m^{-2} h^{-1}]		[mg C m^{-2} h^{-1}]	[µg N m^{-2} h^{-1}]	
year 1	43.41±4.1	10.42±0.6	3.57±0.1	31.57±4.0	6.82±0.5	
	(0.7-177.5)	(-6.3-75.4)	(1.2-5.7)	(0.9-82.8)	(-1.0-48.6)	
year 2	33.00±2.9	10.15±0.4	7.36±0.6	29.23±3.2	7.63±0.5	0.67[1)]±0.1
	(0.2-103.4)	(0 – 41.8)	(0.2-44.9)	(2.9-77.6)	(0.03-37.4)	(0 -2.2)

[1)] Total NO-N loss between August and October 2003.

Table 4. Total measured versus total predicted (bold type) CO_2-C, N_2O-N and NO-N losses (±S. E) at SW and KL in the two investigation years. Predicted values are based on Models 1 to 4.

	SW			KL		
	CO_2	N_2O	NO	CO_2	N_2O	NO
	[kg C ha^{-1} y^{-1}]	[kg N ha^{-1} y^{-1}]		[kg C ha^{-1} y^{-1}]	[kg N ha^{-1} y^{-1}]	
		0.79 ± 0.004	0.24 ± 0.004		0.64 ± 0.014	
year 1	2916 ± 491	**0.75 ± 0.003**	**0.18 ± 0.005**	2413 ± 230	**0.54 ± 0.031**	**0.026 ± 0.002**
		0.79 ± 0.006	0.49 ± 0.038		0.65 ± 0.010	0.021[1)] ± 0.001
year 2	2875 ± 430	**0.82 ± 0.005**	**0.39 ± 0.022**	2315 ± 281	**0.67 ± 0.021**	**0.018 ± 0.001**

[1)] Total NO-N loss between August and October 2003.

Table 5. Monthly mean N_2O and NO emissions in $\mu g\,N\,m^{-2}h^{-1}$ derived from (a) manual chambers (in SW-biweekly, in KL-monthly) and (b) AGPS system (1/day) and the continuous dynamic system (c).

	SW			KL		
	N_2O		NO	N_2O		NO
	(a)	(b)	(c)	(a)	(b)	(c)
Apr-02	7.65			24.59 *		
May-02	16.37			14.17		
Jun-02	27.53 *	18.40	3.13	9.69		
Jul-02	12.86	17.63	3.69	11.90	10.96	
Aug-02	6.35	6.87	3.51	9.68	6.41	
Sep-02	7.89 *	6.04	3.56	3.39	8.07	
Oct-02	7.71	4.42	3.66	4.85	6.27	
Nov-02	9.57	11.91 *		4.18	3.43[3)]	
Dec-02	3.29	17.52[1)]		2.01	14.22[3)]	
Jan-03	2.23	10.74[2)]		0.98	16.33[5)]	
Feb-03	9.27	20.66[3)]		2.15	3.15[5)]	
Mar-03	3.90	5.37		4.63	3.54	
Apr-03	9.45	8.83 **		4.45	3.96	
May-03	7.50	8.81 *	5.49	11.35	5.57	
Jun-03	7.64	5.73 *	4.88 ***	11.82	3.33	0.66
Jul-03	7.65	5.78 *	3.80 ***	4.62	4.63	0.64
Aug-03	7.41	13.09	3.42	5.68	12.47	
Sep-03	19.35	20.35 **	21.22 ***	18.30	9.67	1.04
Oct-03	12.51	7.59	11.31 ***	7.10	7.64	0.29
Nov-03	12.13 *	9.81	6.47	4.42	6.42	
Dec-03	8.43	6.73[2)]	2.08	3.69		
Jan-04	8.21	3.80[4)]	2.64	6.97		
Feb-04	7.37	5.38[2)]				
Mar-04	3.82	3.68		6.68		
Apr-04	1.97	7.72 *			3.50	
May-04	23.56	22.20	3.41		16.01	
Jun-04		12.14				

[1)] n =3; [2)] n =14; [3)] n = 8; [4)] n =9; [5)] n =2; Asterisks marks significant higher values between the sites (* p<0.05, **p<0.01, ***p<0.001).

Table 6. Parameter estimation for the autoregression models 1 to 5 (Eq. 1) to predict lnN_2O and NO emissions from SW and KL.

site		SW	KL	SW	KL	SW+KL
Model		1	2	3	4	5
dependent variable:	y_t	lnN_2O	lnN_2O	NO	NO	NO
Intercept:	β_0	2.9356 ***	6.0238 ***	3.6122 ***	5.0715 *	5.2686 ***
regression coefficients of independent variables:						
(soil moisture)	β_1	-0.0325 **	-0.1028 ***	-0.0757 **	-0.1015 **	-0.0853 ***
(soil temperature)	β_2	-0.0026 **	0.0561 *	0.2086 ***	0.1978 ***	0.0569 **
		0.0139 ***	0.7427 ***			
(CO_2 emission)	β_3					
total R^2:		**0.53**	**0.73**	**0.95**	**0.73**	**0.85**
n		41	23	119	53	172

Sample period is from April 2002–May 2004 and for model 4 from August–October 2003. Regression coefficients are statistically significant at the * p<0.05, ** p<0.01, *** p<0.001 level.

Table 7. Correlation coefficients for significant relationships of monthly mean N-emissions and monthly N-input data at SW and KL. Total N-deposition (Total Ndep) is calculated from the first investigation year when dry deposition was measured.

	SW	KL	SW	KL	SW
	lnN_2O[1)] -manual		N_2O[2)]-AGPS		NO[2)]
TF NO_3^-					
TF NH_4^+		0.30 **		0.32 *	
TF sumN		0.23 *			
STEM NH_4^+		0.24 *		0.50 ***	
STEM NO_3^-		0.37 **		0.76 ***	
STEM N		0.36 **		0.76 ***	
WET_NH_4^+		0.34 ***	0.30 *	0.46 ***	0.35 *
WET_NO_3^-				0.43 ***	
WETsumN		0.28 **		0.43 ***	
DRY_NO_2	-0.50 ***	-0.60 ***		-0.54 **	0.77 ***
DRY_NH_3	0.32 *	0.58 ***			
DRY_sumN		-0.48 ***		-0.60 ***	0.60 ***
Total Ndep		0.43 **		0.65 ***	0.37 *

TF = throughfall, STEM = stemflow, WET = TF + STEM, DRY = dry deposition ([1)] Pearson and [2)] Spearman). Asterisks indicate statistic significance (* $p<0.05$, **$p<0.01$, ***$p<0.001$).

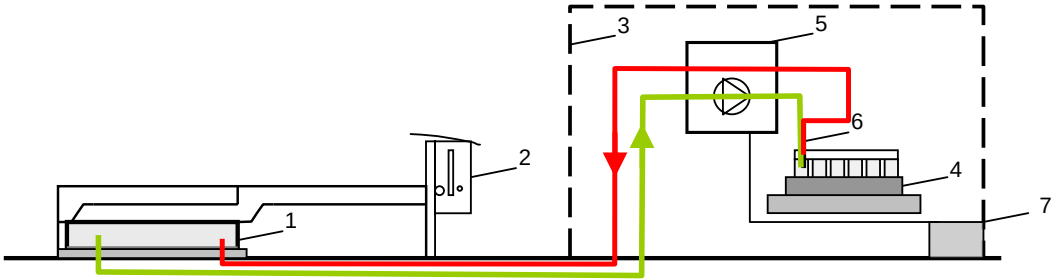

Fig. 1. Schematic of the AGPS with the main components 1) covering case; 2) slipping clutch and a thermostat; 3) protection case; 4) fraction collector; 5) control system, vacuum pump and memory programmable control unit; 6) double needle and 7) power supply.

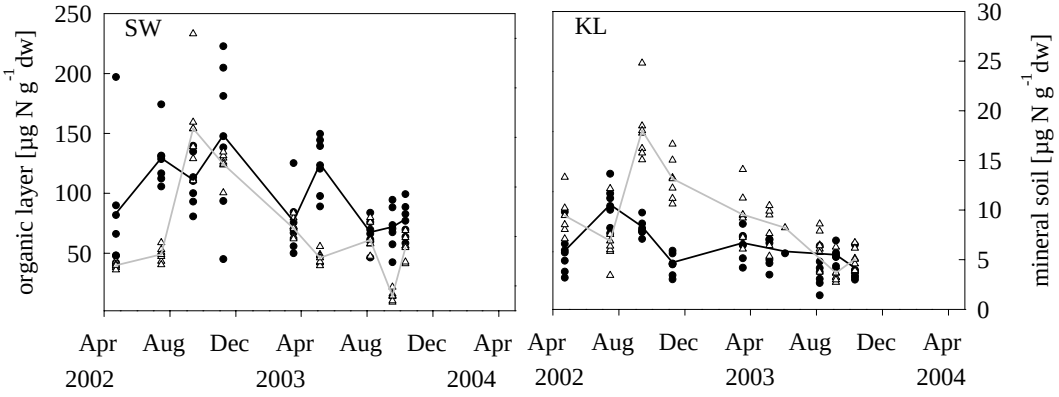

Fig. 2. Extractable soil nitrogen (NH_4^+ and NO_3^-) in the organic layer (circles) and in the mineral soil (0–7 cm) (triangles), at SW and at KL. Pooled samples (n=4) were taken from around the individual chambers.

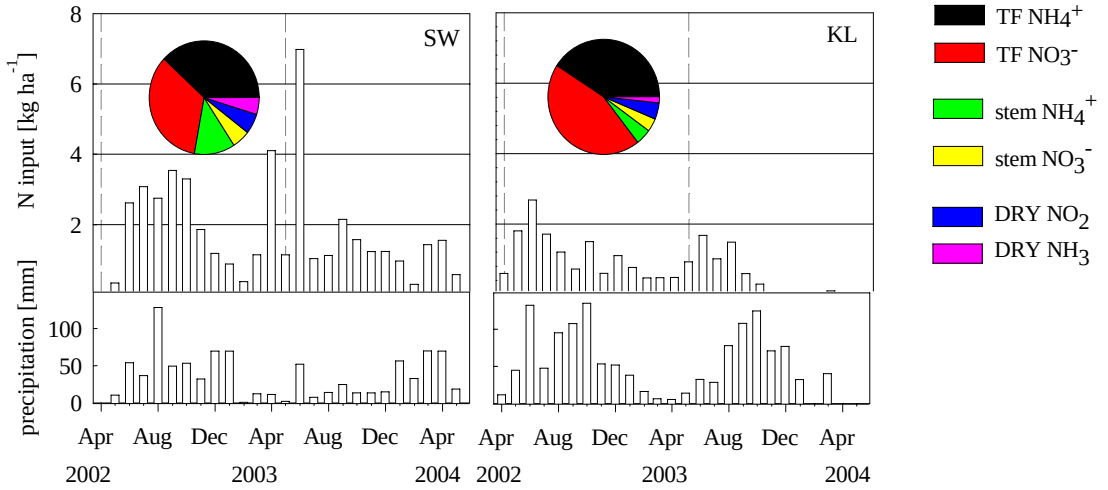

Fig. 3. Bar chart: Monthly N-input (kg N ha^{-1}) and precipitation [mm] at SW and KL for the years 2002–2004. Note: Dry deposition was measured only in the first year. Pie charts: Portion of throughfall (TF NH_4^+, TF NO_3^-), stem-flow (stem NH_4^+, stem NO_3^-), dry deposition (DRY NO_2, DRY NH_3) on annual N-input (kg N ha^{-1}) in the first investigation year.

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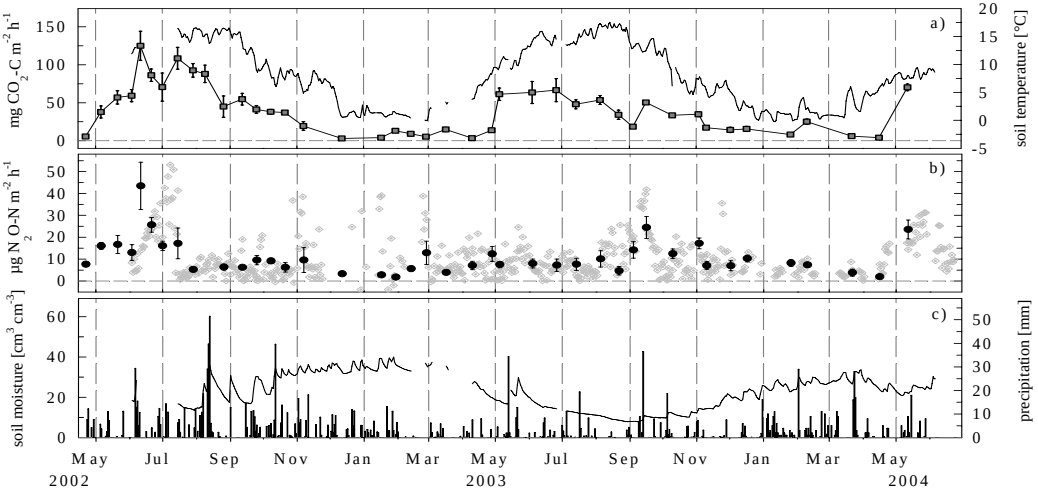

Fig. 4. **(a)** Mean CO_2 emissions (squares±S.E) measured with the manual chambers and soil temperature [5 cm] (black line), **(b)** mean N_2O emissions from manual (circles±S.E) and automatic (diamonds) chambers and **(c)** daily precipitation (from Mariabrunn) and soil moisture [15 cm] at the site SW from April 2002 to June 2004.

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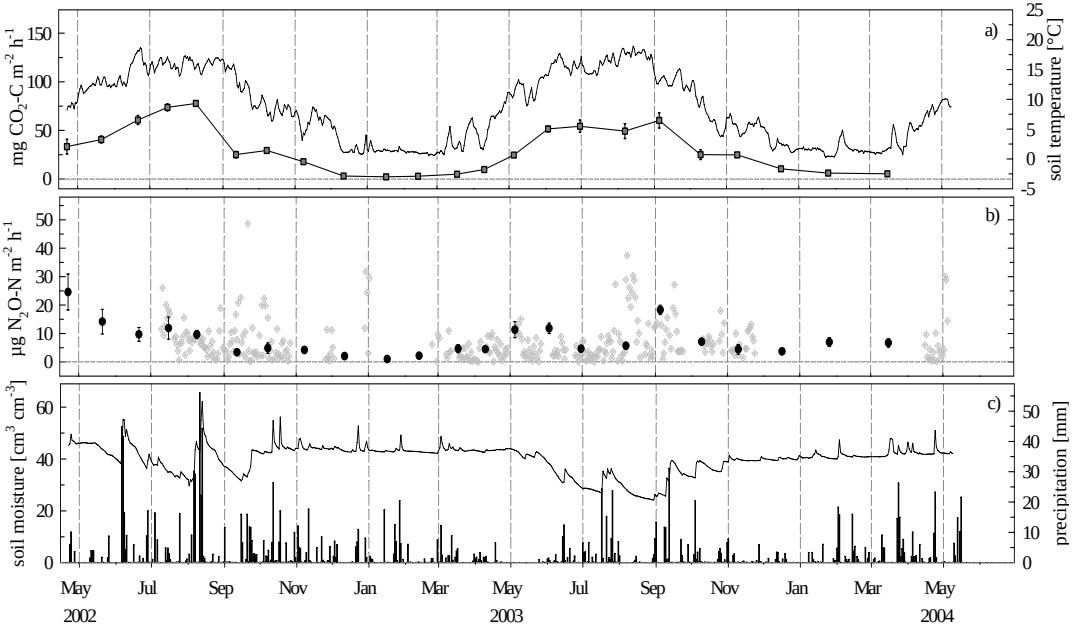

Fig. 5. **(a)** Mean CO_2 emissions (squares±S.E) measured with the manual chambers and soil temperature [5 cm] (black line), **(b)** mean N_2O emissions from manual (circles±S.E) and automatic (diamonds) chambers and **(c)** daily precipitation (at Alland) and soil moisture [15 cm] at the site KL from May 2002 to May 2004.

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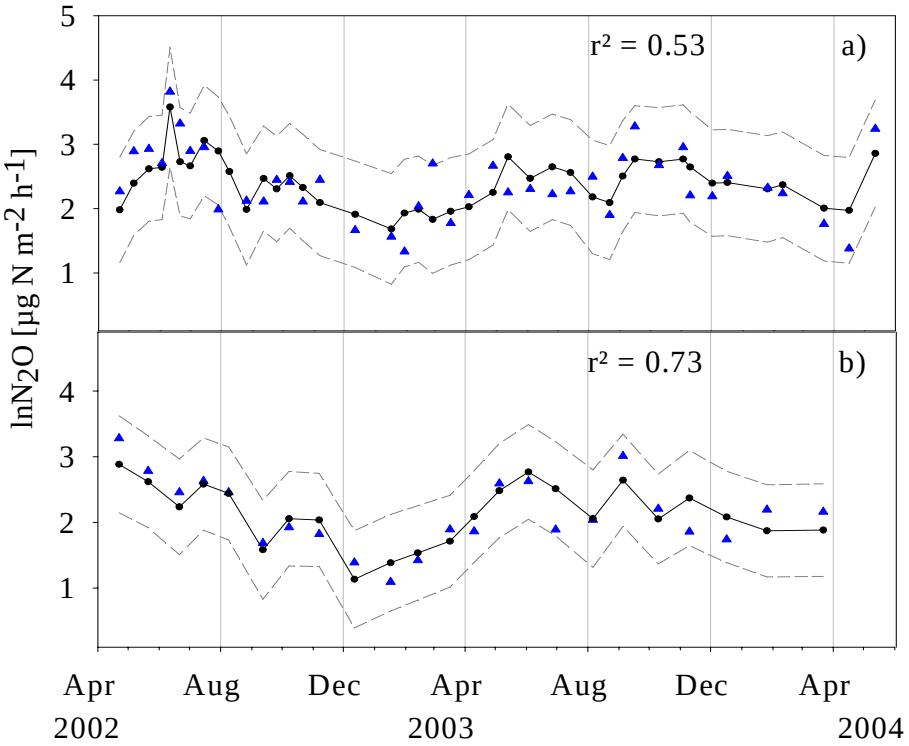

Fig. 6. Measured (triangles), predicted (line with circles) and confidence limits (dashed lines) for log-transformed N_2O emissions in SW **(a)** (Model 1) and KL **(b)** (Model 2) over the investigation years. Independent variables are soil moisture, soil temperature and CO_2 emission for both sites. Autoregressive parameters are shown in Table 6.

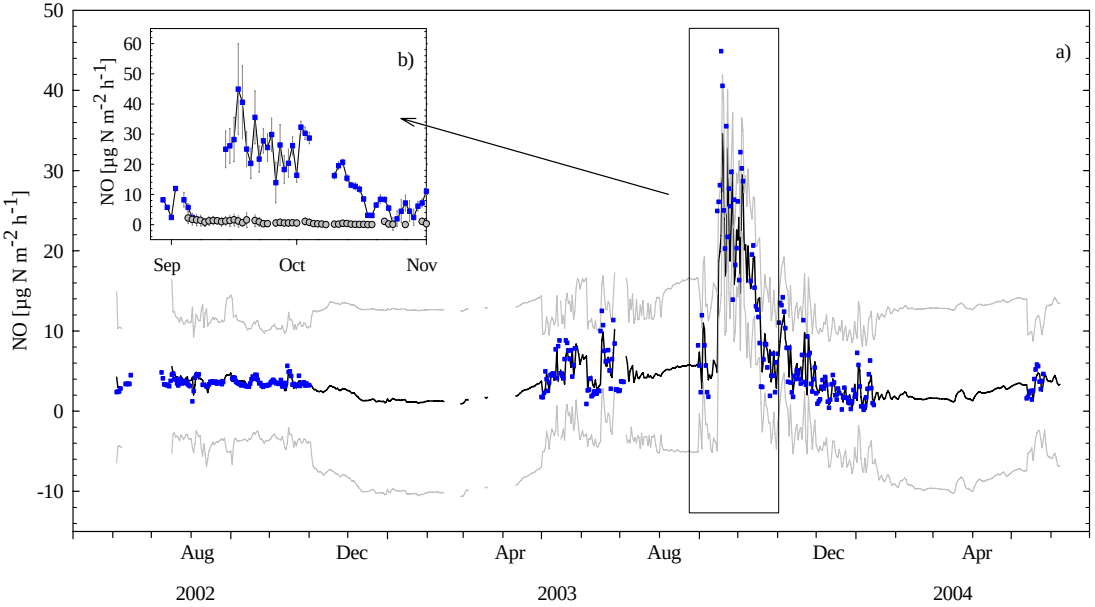

Fig. 7. (a) Measured mean (squares), predicted (black line) and confidence limits (grey line) of NO emission data in SW between 2002 and 2004. Predicted NO emissions are based on observed soil temperature and soil moisture changes (r^2=0.95). Autoregressive parameters for the model (3) are shown in Table 6 **(b)** Comparison of emitted NO±SE in SW (squares) and KL (circles) between August and November 2003.

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